# Decay and slowing down of the multiquanta Davydov-like solitons in molecular chains

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Dynamics and the stability of the multivibron solitons in molecular chains have been examined by means of the perturbation method based upon the inverse scattering transform. We demonstrate that due to the coupling with phonons the soliton radiates energy which causes its slowing down and gradual decay of its amplitude. It was shown that the soliton lifetime depends strongly on temperature and the values of the basic physical parameters of the system. On the basis of these results the possible role of the multivibron solitons in the intramolecular vibrational energy transfer has been critically assessed.

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## I. INTRODUCTION

The long distance charge (electron, proton, ...) and intramolecular vibrational energy transfer is central to chemical and molecular dynamics [1,2] in complex molecules, such as polyacetylene, polypeptide chains ($\alpha$-helix molecule), acetanilide (ACN), etc., where these processes play an important role in a number of phenomena, including metabolism, photochemical reactions (photosynthesis in particular), etc. [1–6]. Therefore the explanation of the transport mechanisms in such molecules is of great importance for the understanding of these phenomena on the microscopic level. A potential solution of the problem, in the context of the resolution of the so-called crisis in bioenergetics [5,6], was proposed by Davydov and co-workers [7,8] who argued that the energy losses of the ''exciton'' (electron, vibron, proton, etc.) through the dispersion and dissipation due to the coupling with environment may be prevented by the self-trapping (ST) of the vibrational energy quanta and formation of the robust, stable, large radius, particlelike entities now commonly known as Davydov solitons (DS) [9,10].

Davydov's ideas have stimulated numerous theoretical and experimental examinations [9–18], sometimes with quite controversial results. Nevertheless, in spite of everything, it is fairly certain now, on the basis of the investigations carried out within the general theory of the ST phenomena [16–18], that the single particle (exciton) soliton cannot be formed and therefore cannot participate in the intramolecular vibrational energy transfer in biopolymers such as $\alpha$ helix and acetanilide (ACN), but still could be relevant for the charge (electron) transfer in these substances. This is a consequence of the smallness of the width of the vibron band in these substances as compared to the maximal phonon frequency (nonadiabatic limit) [9–19]. Under such conditions small-polaron band states should be formed, if ST arise at all, rather than the soliton [11,12]. Quite on the contrary, concerning the electron-phonon interaction, the adiabaticity condition in these systems is satisfied and the soliton formation is allowed on account of the single electron ST [18]. Nevertheless, intramolecular vibrational energy transfer in these substances by means of the solitonic mechanism cannot be excluded totally. However, the original idea must be revised and founded upon the multiquanta soliton as the transfer mechanism. The possibility of the formation of such solitons was discussed recently in Ref. [19] where it was shown that the effective, phonon-mediated, vibron-vibron interaction may lead to the soliton formation even in these systems.

In our previous publications we have examined, within the framework of the mean-field method, the conditions for the creation of such a multiquanta (i.e., multivibron) soliton dependent on the values of the system parameters and temperature [19], the possibility of its experimental verification due to the specific soliton-induced modifications of the phonon spectrum arising on account of the ''dressing'' effect [20], and their kinetic properties [21]. However, in applications to realistic physical systems, the crucial problem is the examination of its stability under the influence of various perturbations that can arise during its motion. In the present paper we shall focus ourselves on the examination of the stability of such solitons and we shall calculate its lifetime using the perturbative treatment based upon the inverse scattering transform (IST) formalism [22–25].

## II. MODEL

The starting point of our analysis is the model Lagrangian of the system derived in our previous paper [21]

$$\mathcal{L}=\frac{i\hbar}{2}\int_{-\infty}^{\infty}\frac{dx}{R_0}(\dot{\beta}\beta^*-\beta\dot{\beta}^*)-\mathcal{H}_s-\mathcal{H}_i+\mathcal{L}_{ph}. \qquad (1)$$

Here $\mathcal{H}_s$ represents the Hamilton's function of the solitonic subsystem which, as shown in [21], may be approximated by the Hamiltonian of the nonlinear Schrödinger model (NSM)

$$\mathcal{H}_s=(\Delta-E_B-2J_{eff})\int_{-\infty}^{\infty}\frac{dx}{R_0}|\beta|^2 + J_{eff}\,R_0^2\int_{-\infty}^{\infty}\frac{dx}{R_0}|\beta_x|^2-2E_B\int_{-\infty}^{\infty}\frac{dx}{R_0}|\beta|^4, \qquad (2)$$

while

$$\mathcal{H}_i=\frac{J_{eff}R_0}{\sqrt{N}}\sum_q\int_{-\infty}^{\infty}\frac{dx}{R_0}\frac{iqR_0F_q}{\hbar\omega_q}e^{iqx}\times(a_q^{\dagger}-a_{-q})(\beta^*\beta_x-\text{c.c.}) \qquad (3)$$

 

denotes the soliton-phonon interaction Hamiltonian. As usual dots and subscripts denote derivation in respect to $t$ and $x$, respectively. Finally

$$\mathcal{L}_{ph}=\frac{i\hbar}{2}\sum_q (\dot{a}_q^\dagger a_q-\mathrm{H.c.})-H_{ph} \tag{4}$$

denotes a phonon subsystem Lagrangian. Here we use the same notation as in Refs. [19–21] so that $a_q^\dagger$ and $a_q$ are the phonon creation and annihilation operators, $\beta\equiv\beta(x,t)$ represents the soliton amplitude, and $F_q$ is the exciton-phonon coupling parameter. It is given as $F_q=2i\chi(\hbar/2M\omega_q)^{1/2}\sin qR_0$ in the case of coupling with acoustic phonons with frequency $\omega_q=\omega_B\sin|qR_0/2|$, and as $F=\chi(\hbar/2M\omega_0)^{1/2}$ for the coupling with the dispersionless optical phonons with frequency $\omega_q=\omega_0\equiv$const. Here $\omega_B=2(\kappa/M)^{1/2}$ denotes the maximal acoustic phonon frequency, $\kappa$ is the spring constant, $M$ denotes the mass of the molecular group, $R_0$ denotes the lattice constant. The energy spectrum of the system is determined by the following parameters: vibron excitation energy $(\Delta)$, small-polaron binding energy $[E_B=(1/N)\Sigma_q(|F_q|^2/\hbar\omega_q)]$, and finally the effective intersite transfer integral $(J_{eff}=Je^{-S(T)})$. Here

$$S(T)=\frac{2}{N}\sum_q \frac{|F_q|^2}{(\hbar\omega_q)^2}\sin^2\frac{qR_0}{2}(2\overline{\nu}_q+1)$$

denotes the temperature-dependent coupling constant introduced in [16,18] ($\overline{\nu}_q$ is the equilibrium phonon distribution).

The above model Lagrangian describes the system consisting of the classical particle(s)—multiquanta soliton(s) interacting with the quantum-mechanical thermal bath (phonons). It was derived assuming that the soliton existence condition [19]

$$S(T)<\frac{B(T)}{\mathcal{N}} \tag{5}$$

is satisfied. Here $B(T)=(8/3\pi)(2J/\hbar\omega_B)[S(T)/S(0)]$ denotes the temperature-dependent adiabaticity parameter. Since we are primarily interested in the substances such as ACN and $\alpha$ helix, for which system parameters belong to the nonadiabatic region $(B<1)$, the above condition implies that the soliton existence is allowed if $S\ll 1$. For that reason the perturbative treatment based upon the IST method is justified.

In order to calculate the soliton lifetime we shall analyze the perturbed nonlinear Schrödinger equation (NSE) arising in the standard way from the above model Lagrangian,

$$\begin{aligned} i\hbar\dot{\beta}(x,t)+J_{eff}R_0^2\beta_{xx}(x,t)+4E_B|\beta(x,t)|^2\beta(x,t)\\ =f_1(x,t)\beta(x,t)+f_2(x,t)\beta_x(x,t). \end{aligned} \tag{6}$$

The irrelevant term $(\Delta-2J_{eff}-E_B)\beta(x,t)$ is removed by the simple phase transformation

$$\tilde{\beta}(x,t)=e^{i[(\Delta-2J_{eff}-E_B)t/\hbar]}\beta(x,t).$$

Here $f_1(x,t)$ and $f_2(x,t)$ are fluctuation forces due to the coupling with phonons. They are explicitly given as follows:

$$f_1(x,t)=\frac{J_{eff}}{\sqrt{N}}\sum_q \frac{F_q q^2R_0^2}{\hbar\omega_q}e^{iqx}[a_{-q}(t)-a_q^\dagger(t)], \tag{7}$$

$$f_2(x,t)=\frac{2iJ_{eff}}{\sqrt{N}}\sum_q \frac{F_q qR_0^2}{\hbar\omega_q}e^{iqx}(a_q^\dagger(t)-a_{-q}(t)). \tag{8}$$

Here, in accordance with the assumption of the weak soliton-phonon coupling, we may regard that the phonon subsystem is practically unaffected by this interaction and consequently, the time dependence of phonon operators in Eqs. (7) and (8) simply denotes the interaction picture with respect to the phonon Hamiltonian. In other words, $a_q(t)=a_qe^{-i\omega_qt}$, $a_q^\dagger(t)=a_q^\dagger e^{i\omega_qt}$. Thus one may take that the phonon subsystem is in the thermal equilibrium and the correlation functions of these forces are

$$\begin{aligned} \langle f_1(x,t)f_1^\dagger(x',t')\rangle=\frac{4J_{eff}^2S}{N}\sum_q (qR_0)^3e^{iq(x-x')}\\ \times[\overline{\nu}_qe^{i\omega_q(t-t')}+(1+\overline{\nu}_q)e^{-i\omega_q(t-t')}], \end{aligned} \tag{9}$$

$$\begin{aligned} \langle f_2(x,t)f_2^\dagger(x',t')\rangle=\frac{16J_{eff}^2S}{N}\sum_q qR_0^3e^{iq(x-x')}[\overline{\nu}_qe^{i\omega_q(t-t')}\\ +(1+\overline{\nu}_q)e^{-i\omega_q(t-t')}]. \end{aligned} \tag{10}$$

Equation (6) has the similar form as the one considered recently by Flytzanis *et al.* [24] who examined the radiative decay of the one-dimensional adiabatic acoustic polaron. Their results enable one to estimate the possible role of the original Davydov concept for the charge (electron) transfer in molecular chains. As compared with that study the only difference we have here is the nature of the ‘‘random’’ forces which are now the quantum-mechanical operators. However, during the practical calculations we shall encounter the mean values of the product of these forces, so that this difference is irrelevant, and the only condition that must be satisfied is the smallness of the external forces. This condition is satisfied as can be seen from the magnitude of the above correlators that are proportional to the coupling constant, which is small in the soliton sector for the system we are dealing with. Therefore, in further calculations we may follow, as closely as possible, the procedure utilized in [24,25]. As a first step we rewrite Eq. (6) in the dimensionless form which is convenient for the practical calculations. Using the new variables $z=x/R_0$, $\tau=(J_{eff}/\hbar)t$, $Q=qR_0$, perturbed NSE (6) attains the simple form:

$$i\psi_\tau(z,\tau)+\psi_{zz}(z,\tau)+2|\psi(z,\tau)|^2\psi(z,\tau)=\mathcal{R}(z,\tau). \tag{11}$$

Here the nonlinearity parameter $2E_B/J_{eff}$ was absorbed into the scaled amplitude $\psi(z,\tau)=\sqrt{2E_B/J_{eff}}\beta(x,t)$. The term on the right-hand side which defines perturbation is specified as

$$\mathcal{R}(z,\tau)=f_1(z,\tau)\psi(z,\tau)+f_2(z,\tau)\psi_z(z,\tau). \tag{12}$$

In this equation $f_1(z,\tau)$ and $f_2(z,\tau)$ are the random forces (7) and (8) written in the dimensionless units

$$f_1(z,\tau)=\sum_Q \sum_{j=\pm 1} A_j(Q)e^{ijc|Q|\tau}e^{iQz}, \tag{13}$$

$$f_2(z,\tau)=\sum_Q \sum_{j=\pm 1} B_j(Q)e^{ijc|Q|\tau}e^{iQz},$$

where the operator functions are explicitly given as

$$A_1(Q)=\frac{-1}{\sqrt{N}}\frac{F_Q Q^2}{\hbar\omega_Q}a_Q^{\dagger}, \quad A_{-1}(Q)=\frac{1}{\sqrt{N}}\frac{F_Q Q^2}{\hbar\omega_Q}a_{-Q}, \tag{14}$$

$$B_1(Q)=2i\frac{1}{\sqrt{N}}\frac{F_Q Q}{\hbar\omega_Q}a_Q^{\dagger}, \quad B_{-1}(Q)=2i\frac{-1}{\sqrt{N}}\frac{F_Q Q}{\hbar\omega_Q}a_{-Q}.$$

Correlators of the above random forces are defined as

$$\langle f_1(z,\tau)f_1^{\dagger}(z',\tau')\rangle=\frac{4S}{N}\sum_Q Q^3 e^{iQ(z-z')}[\overline{\nu_Q}e^{ic|Q|(\tau-\tau')} + (1+\overline{\nu_Q})e^{-ic|Q|(\tau-\tau')}], \tag{15}$$

$$\langle f_2(z,\tau)f_2^{\dagger}(z',\tau')\rangle=\frac{16S}{N}\sum_Q Q e^{iQ(z-z')}[\overline{\nu_Q}e^{ic|Q|(\tau-\tau')} + (1+\overline{\nu_Q})e^{-ic|Q|(\tau-\tau')}], \tag{16}$$

In the above equations, in the same way as in [24], we have introduced the dimensionless speed of sound $c=(\hbar\omega_B/2J_{eff})\approx 1/B$. Obviously, for the systems we are dealing with $c \gg 1$.

## III. SOLITON DECAY AND SLOWING DOWN

In the absence of perturbation, NSE is exactly integrable and besides the known soliton solution it also has the set of delocalized linear solutions that form the continuum, the so-called ''exciton,'' band. In the context of IST theory these linear modes are usually called radiation fields [22,23]. Due to the exact integrabilty of the NSE, the unperturbed model has an infinite set of the integrals of motion, each consisting of the two parts corresponding to the soliton and the continuum branch of the spectrum, respectively. In the present context only the first two are interesting for us. This is the norm (number of quanta)

$$\mathcal{N}=\int_{-\infty}^{\infty}dz|\psi(z,\tau)|^2=4\eta+\int_{-\infty}^{\infty}d\lambda|\mathcal{B}(\lambda)|^2 \tag{17}$$

and field momentum

$$P=\frac{i}{2}\int_{-\infty}^{\infty}dz(\psi_z(z,\tau)\psi^*(z,\tau)-\text{c.c.}) =2\eta V+\int_{-\infty}^{\infty}2\lambda|\mathcal{B}(\lambda)|^2 d\lambda. \tag{18}$$

The first terms in the above expressions, proportional to $\eta$, come from the normalization of the soliton solution,

$$\psi_{sol}=\frac{2i\eta e^{i[(Vz)/2+(4\eta^2-V^2/4)\tau-\phi_0]}}{\cosh[2\eta(z-V\tau)-z_0]} \tag{19}$$

and denote the soliton norm and momentum, respectively. The second terms in Eqs. (17) and (18) come from the continuum component and denote the number of the emitted quanta (17) and the momentum of the radiation field (18). Here $V=v\hbar/J_{eff}R_0$ is the soliton velocity in dimensionless units ($v$ is the real soliton velocity). Note that the original Hamiltonian from which our model Lagrangian (1)–(4) has been derived [21] does not include the anharmonic terms in the Hamiltonian of the phonon subsystem, which are necessary for the examination of the so-called ''supersonic'' solitons [26]. Consequently, our further analysis concerns the subsonic case ($V<c$ or $v<c_0$). Quantity $\mathcal{B}(\lambda,\tau) \equiv b(\lambda,\tau)e^{-4i\lambda^2\tau}$ may be calculated by virtue of the expression [22]

$$\frac{d\mathcal{B}}{d\tau}=-e^{-4i\lambda^2\tau}a(\lambda)\int_{-\infty}^{\infty}dz\{[\Psi^{(1)*}(z,\lambda)]^2\mathcal{R}^*(z) +[\Psi^{(2)*}(z,\lambda)]^2\mathcal{R}(z)\}. \tag{20}$$

Here $\Psi^{(1,2)}(\lambda,\tau)$ stands for the two-component one-soliton Jost function for the NSE, while $b(\lambda)$ denotes the IST reflection coefficient. In the absence of the external field both the soliton amplitude and the velocity are constant in time. Under the influence of the external forces soliton parameters evolve in time. In particular, the perturbation may induce coupling between the two independent branches, soliton and radiation, of the spectrum of NSM. This in turn may cause the ''particles'' exchange between them which finally leads to the soliton decay and slowing down. In order to study these effects, let us differentiate with respect to time the averaged (averaging is taken over the equilibrium phonon ensemble) equations (17) and (18). In such a way and, having in mind that the number of quanta is conserved ($d\mathcal{N}/d\tau=0$), from Eq. (17) we easily obtain the mean soliton decay rate

$$\frac{d\eta}{d\tau}=-\frac{1}{4}\int_{-\infty}^{\infty}\mathcal{P}(\lambda)d\lambda. \tag{21}$$

Soliton slowing down may be analyzed with the help of the equation

$$\frac{d(\eta V)}{d\tau}=-\int_{-\infty}^{\infty}\lambda\mathcal{P}(\lambda)d\lambda, \tag{22}$$

which may be derived in the same way as the preceding equation.

In further analysis our primary task is to calculate the mean spectral density (MSD) of the radiation field: $\mathcal{P}(\lambda) =(2/\pi)\mathrm{Re}\langle\mathcal{B}^*(\lambda,\tau)d\mathcal{B}(\lambda,\tau)/d\tau\rangle$. It can be done with the help of Eq. (20) from which one may find the desired quantity $\mathcal{B}(\lambda)$ and its time derivative. Substituting the explicit form of the single soliton Jost functions [Eqs. (A3) and (A4) in [22]] into Eq. (20) and performing the integration over $z$, we arrive at

$$\frac{d\mathcal{B}(\lambda)}{d\tau}=\frac{\pi}{\left(\lambda+\frac{V}{4}\right)^2+\eta^2}\sum_Q\sum_{j=\pm1}\frac{e^{if(Q,\lambda,\eta)\tau}}{\cosh\frac{Q-2\lambda-\frac{V}{2}}{4\eta}\pi}[iA_j(Q)a_1(\lambda,\eta)+VB_j(Q)a_2(\lambda,\eta)], \tag{23}$$

where $f(Q,\lambda,\eta)=jc|Q|-4(\lambda^2+\eta^2)+QV-2\lambda V-V^2/4$, $a_1=3(\lambda+V/4)^2-Q(\lambda+V/4)-\eta^2$, and $a_2=-(\lambda+V/4)^2+Q^2/8$. In order to find $\mathcal{B}(\lambda)$ we use the procedure as in [25]. That is, we first multiply the above equation by $e^{\alpha\tau}$, and in some later stage the limit $\alpha\to0$ will be taken. This trick corresponds to adiabatically turning on the perturbation which was absent at $\tau=-\infty$. In such a way we obtain

$$\mathcal{B}^+(\lambda)=\frac{\pi^2}{\left(\lambda+\frac{V}{4}\right)^2+\eta^2}\sum_Q\sum_{j=\pm1}\frac{e^{-if(Q,\lambda,\eta)\tau}}{\cosh^2\frac{Q-2\lambda-\frac{V}{2}}{4\eta}\pi}[-iA_j^\dagger(Q)a_1(\lambda,\eta)+VB_j^\dagger(Q)a_2(\lambda,\eta)]\delta(f(Q,\lambda,\eta)). \tag{24}$$

In deriving this expression we have used the identity $\lim_{\alpha\to0}(x\pm i\alpha)^{-1}=\mathrm{P}(1/x)\mp i\pi\delta(x)$ (P denotes the principal value). Combining the last two equations we obtain the following expression for the MSD of the radiation field:

$$\mathcal{P}(\lambda)=\frac{2\pi^2}{\left[\left(\lambda+\frac{V}{4}\right)^2+\eta^2\right]^2}\sum_{Q',Q}\sum_{j',j=\pm1}\frac{a_1^2(\lambda,\eta)\langle A_j^\dagger(Q)A_{j'}(Q')\rangle+V^2a_2^2(\lambda,\eta)\langle B_j^\dagger(Q)B_{j'}(Q')\rangle}{\cosh^2\frac{Q-2\lambda-\frac{V}{2}}{4\eta}\pi}\delta(f(Q',\lambda,\eta)). \tag{25}$$

Performing the above denoted averaging over the phonon ensemble and replacing the summation over $Q$ by the integration in accordance with the rule $(1/N)\Sigma_Q\cdots=(1/2\pi)\int_{-\pi}^{\pi}dQ\cdots$ the last expression becomes

$$\mathcal{P}(\lambda)=\frac{\pi}{\left[\left(\lambda+\frac{V}{4}\right)^2+\eta^2\right]^2}\sum_{j=\pm1}\int_{-\pi}^{\pi}dQ\frac{|F_Q|^2}{(\hbar\omega_Q)^2}\frac{(2\nu_Q+1)(a_1^2Q^4+V^2Q^2a_2^2)}{\cosh^2\frac{q-2\lambda-\frac{V}{2}}{4\eta}\pi}\delta\left((c+jV)Q-4j(\lambda^2+\eta^2)-2j\lambda V-j\frac{V^2}{4}\right). \tag{26}$$

Integrals over $Q$ in the above expression may be evaluated easily due to the presence of the $\delta$ function. In such a way we obtain a quite cumbersome expression for $\mathcal{P}(\lambda)$ which is not convenient for further analysis. In particular, thus obtained, the exact expression for the spectral density is a very complicated function of the radiation field wave vector ($\lambda$) so that the evaluation of the integrals over $\lambda$, which must be found for the calculation of the average soliton decay rate, is quite difficult, and, in general, it cannot be found in closed form analytically. For that reason we have to introduce some reasonable approximation. In particular, in the high and low temperature case it can be satisfactory estimated by means of the approximations proposed before [22–25].

### A. High temperature limit

In this case the phonon average number may be taken as $\nu_q\approx kT/\hbar\omega_q$, and after the substitution of the explicit $Q$ dependence of the system parameters we have

$$\mathcal{P}(\lambda)=\frac{16\pi SkT}{\hbar\omega_B}\frac{1}{[\tilde\lambda^2+\eta^2]^2}\times\int_{-\pi}^{\pi}dQ\frac{(a_1^2Q^2+V^2a_2^2)}{\cosh^2\frac{Q-2\tilde\lambda}{4\eta}\pi}\times\sum_{j=\pm1}\frac{1}{|c+jV|}\delta\left(Q-4j\frac{\tilde\lambda^2+\eta^2}{c+jV}\right). \tag{27}$$

Here $\tilde\lambda=\lambda+V/4$ and in what follows the tilde will be omitted. Performing the desired integration we obtain the following expression for the MSD:

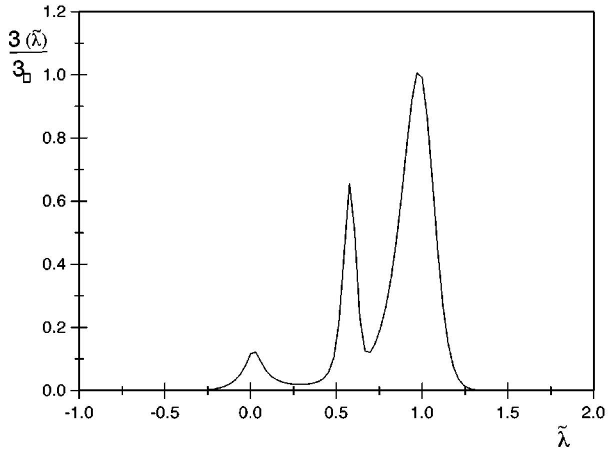


FIG. 1. Average spectral density of the radiation field, measured in units of $\mathcal{P}_0=(16\pi SkT/\hbar\omega_B)$ for $V=c/4$ and $\eta=0.1$ versus the dimensionless radiation field wave vector $\tilde{\lambda}=(\lambda/\lambda_1)$. High temperature limit.

$$\mathcal{P}(\lambda)=\frac{16\pi SkT}{\hbar\omega_B}\sum_{j=\pm1}\times\frac{R_1(\lambda)+R_2(\lambda)}{|c+jV|\cosh^2\frac{2\lambda^2-(c+jV)\lambda+2\eta^2}{2\eta(c+jV)}\pi},\quad(28)$$

where $R_i(\lambda)$ stands for the following polynomials:

$$R_1(\lambda)=\frac{16}{(c+jV)^2}\left[9\lambda^4-\frac{24\lambda^3(\lambda^2+\eta^2)}{c+jV}+\frac{16\lambda^2(\lambda^2+\eta^2)^2}{(c+jV)^2}+\frac{8\lambda(\lambda^2+\eta^2)\eta^2}{c+jV}-6\lambda^2\eta^2+\eta^4\right],\quad(29)$$

$$R_2(\lambda)=\frac{V^2}{(\lambda^2+\eta^2)^2}\left[\lambda^4-\frac{4\lambda^2(\lambda^2+\eta^2)^2}{(c+jV)^2}+\frac{4(\lambda^2+\eta^2)^4}{(c+jV)^4}\right].\quad(30)$$

For the estimation of the soliton life time one should calculate the total mean radiation power $\int_{-\infty}^{\infty}\mathcal{P}(\lambda)d\lambda$. Unfortunately, the desired integration cannot be performed exactly. However, according to the explicit form of $\mathcal{P}(\lambda)$ (see Fig. 1), these integrals may be fairly good estimates in accordance with the procedure proposed in Refs. [22–25].

As one can see $\mathcal{P}(\lambda)$ is highly peaked in the vicinity of the points $\lambda_{1,2}^{(j)}=[c+jV\pm\sqrt{(c+jV)^2-16\eta^2}]/4$ corresponding to the zeros of the argument of $\cosh^2 g(\lambda)$ in the last expression, while the peak falling onto $\lambda=0$ is substantially lower. Since we are dealing with the nonadiabatic case $c\gg1$ we have $c\gg\eta$ so that the $\mathcal{P}(\lambda)$ has two pronounced maxima at $\lambda_j=(c+jV)/2$. When $\lambda\gg\lambda_j$ spectral density decreases exponentially so that the main contribution in the desired integrals comes from the $\lambda$ in the vicinity of these points. Obviously the contribution from the third peak may be disregarded. Thus we may approximate these integrals by $\Sigma_{j=1,2}\mathcal{P}(\lambda_j)\Delta\lambda$, where $\Delta\lambda$ stands for the width of these maxima, which is proportional to the soliton amplitude, i.e., $\Delta\lambda\sim\eta$. It was estimated analyzing the behavior of the $\cosh^{-2}g(\lambda)$ that mainly determine the shape of $\mathcal{P}(\lambda)$. Thus, looking for the width of that distribution at half of its maximal value we found $\Delta\lambda$ ($\Delta\lambda\ll\lambda_j$) from the equation $\cosh^{-2}[g(\lambda_j+\Delta\lambda/2)]=1/2$.

In such a way we obtain the following estimate for the average soliton decay rate in the real units

$$\frac{d\eta}{dt}=-\Gamma(v)\eta,\quad(31)$$

where $\Gamma(v)$ denotes a velocity-dependent damping constant given as

$$\Gamma(v)=\gamma\left[1-\frac{1}{4(v^2/c_0^2-1)}\right],\quad(32)$$

where $\gamma=8\pi SkTc_0/\hbar\omega_B R_0$. In an analogous way we have calculated the integral $\int_{-\infty}^{\infty}\lambda\mathcal{P}(\lambda)d\lambda$ so that Eq. (22) becomes

$$\frac{d(\eta v)}{dt}=-2\gamma\eta v.\quad(33)$$

Thus the above IST equations, after some manipulations, result in the following system equations for the soliton parameters in real units:

$$\frac{dv}{dt}=-\gamma\left[1-\frac{c_0^2}{4(c_0^2-v^2)}\right]v,\quad(34)$$

$$\frac{d\eta}{dt}=-\gamma\left[1+\frac{c_0^2}{4(c_0^2-v^2)}\right]\eta.\quad(35)$$

Equation (34) may be integrated easily and we obtain the following expression for the time dependence of the soliton velocity:

$$\frac{v}{\left(1-\frac{4v^2}{3c_0^2}\right)^{1/8}}=\frac{v_0e^{-(3/4)\gamma t}}{\left(1-\frac{4v_0^2}{3c_0^2}\right)^{1/8}},\quad(36)$$

where $v_0<0.87c_0$ represents the initial soliton velocity. It is easy to show that this expression represents an equation of the fourth order of $v^2$, which can be solved explicitly. However, the resulting solution represents a very complicated function of the soliton velocity on time which is not very convenient for practical analysis. Therefore, from this equation we find $t$ as a function of velocity:

$$\mathcal{T}=-\ln\left[\frac{v}{v_0}\left(\frac{1-\frac{4v_0^2}{3c_0^2}}{1-\frac{4v^2}{3c_0^2}}\right)^{1/8}\right],\quad(37)$$

which may be simply inverted to find the desired time dependence of the soliton velocity. It is given explicitly in Fig. 2 where we have plotted, for the two values of $v_0$, the dependence of the soliton velocity (measured in units of $v_0$) on

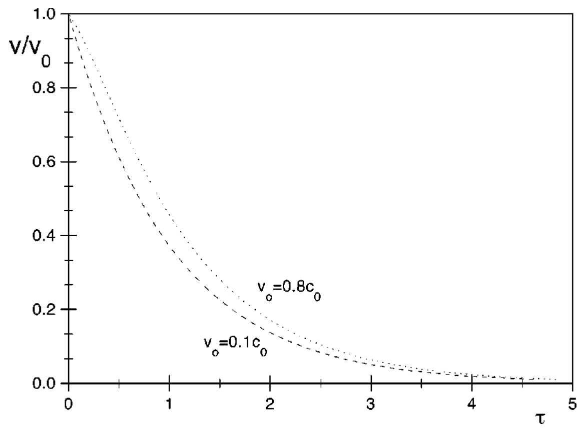


FIG. 2. Soliton velocity measured in units of $v_0$ versus the dimensionless time $\mathcal{T}$. High temperature limit.

dimensionless time $\mathcal{T}$ ($\mathcal{T}=\frac{3}{4}\gamma t$). Here the dashed and dotted lines correspond to $v_0=0.1c_0$ and $v_0=0.8c_0$, respectively. It follows that the soliton velocity exponentially decreases.

Time dependence of the soliton amplitude, necessary for the estimation of its lifetime, may be found with the help of the auxiliary relation: $\eta v=\eta_0 v_0 e^{-2\gamma t}$, which follows from Eq. (33) for $v<c_0$. Here $\eta_0=E_B/2J_{eff}$ denotes the soliton initial amplitude. Inserting this relation in the expression for $\mathcal{T}$ we obtain the following equation for the soliton amplitude:

$$z^4+\frac{a}{1-a}ze^{6\gamma t}-\frac{1}{1-a}e^{10\gamma t}=0, \tag{38}$$

where $z=(\eta_0/\eta)^2$, $a=4v_0^2/3c_0^2$, $b=e^{8\gamma\mathcal{T}/a-1.}$ It can be solved explicitly so we have

$$\eta=\eta_0\sqrt{2\left(\sqrt{\frac{2b}{\sqrt{y}}-y}-\sqrt{y}\right)^{-1}}, \tag{39}$$

where

$$y=\frac{e^{20\mathcal{T}/3}}{2^{1/3}(a-1)^{2/3}}y_1^{1/6}\left[\left(1+\frac{e^{-4\mathcal{T}}}{y_1}\right)^{1/3}-\left(1-\frac{e^{-4\mathcal{T}}}{y_1}\right)^{1/3}\right], \tag{40}$$

and

$$y_1=\left[\frac{256}{27}a^3(a-1)+e^{-8\mathcal{T}}\right]. \tag{41}$$

These results are visualized in Fig. 3, which represent dependence of the $\eta/\eta_0$ on $\mathcal{T}$, for the two above chosen values of $v_0$. In particular, the dashed and dotted lines correspond to $v_0=0.1c_0$ and $v=0.8c_0$, respectively. The full line corresponds to a pure exponential curve: $\eta=\eta_0 e^{-5\mathcal{T}/3}$, here introduced for comparison. As one can see the soliton amplitude decreases approximately following the pure exponential law. On the basis of these predictions one may estimate the soliton half-life time as follows:

$$\tau_{1/2}\sim\frac{4\ln 2}{5\gamma}=3.39(\mathrm{ST})^{-1}\times 10^{-13}\ \ \mathrm{s}. \tag{42}$$

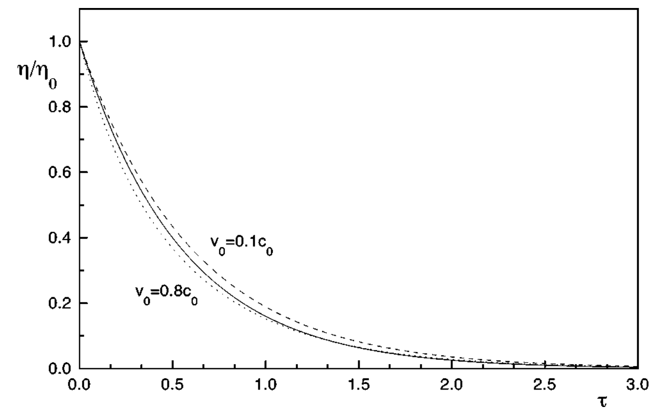


FIG. 3. Decay of the soliton amplitude versus the dimensionless time: $\mathcal{T}$. High temperature limit.

### B. Low temperature limit

In this case the phonon average number practically vanishes and we obtain

$$\mathcal{P}(\lambda)=\frac{4\pi S}{(\tilde{\lambda}^2+\eta^2)^2}\int_{-\pi}^{\pi}|Q|dQ \times\frac{(a_1^2Q^2+V^2a_2^2)}{\cosh^2\frac{Q-2\tilde{\lambda}}{4\eta}\pi}\sum_{\pm 1}\frac{1}{|c+jV|}\delta\left(Q-4\frac{\tilde{\lambda}^2+\eta^2}{c+jV}\right). \tag{43}$$

This expression corresponds to Eq. (28) in the high temperature limit calculations. Note that $\tilde{\lambda}$ has the same meaning as before so that in what follows the tilde may be omitted. Strictly following the procedure as in the previous case we obtain the following expression for the MSD of the radiation:

$$\mathcal{P}(\lambda)=16\pi S\sum_{j=\pm 1}\frac{(\lambda^2+\eta^2)[R_1(\lambda)+R_2(\lambda)]}{(c+jV)^2\cosh^2\frac{2\lambda^2-(c+jV)\lambda+2\eta^2}{2\eta(c+jV)}\pi}. \tag{44}$$

To find the soliton decay rate we shall use the similar approximations as those involved in the deriving of Eq. (29).

For that purpose we plot the low temperature MSD (Fig. 4), which behaves in the same way as well as in the high temperature limit. Thus one safely may follow the same procedure as before and we found that the average soliton amplitude and product $\eta v$ satisfy the following system:

$$\frac{d\eta}{dt}=-2G\left(1+\frac{5v^2}{4c_0^2}\right)\eta, \tag{45}$$

$$\frac{d(\eta v)}{dt}=-2Gc_0\left(1+\frac{13v^2}{4c_0^2}\right)\eta. \tag{46}$$

Combining these two equations we finally obtain the following evolution equation for the soliton velocity in the low temperature limit:

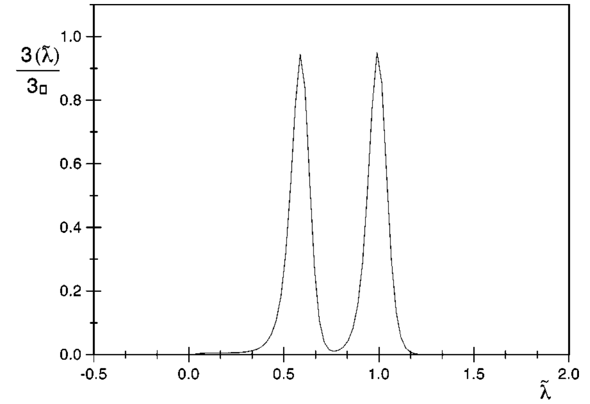


FIG. 4. Average spectral density of the radiation, measured in units of $\mathcal{P}_0=16\pi S$, versus the dimensionless radiation field wave vector: $\tilde{\lambda}=\lambda/\lambda_1$, for $V=c/4$ and $\eta=0.1$. Low temperature limit.

$$\frac{dy}{dt}=-G(1+13y^2-2y-10y^3), \tag{47}$$

where $y=v/2c_0$ and $G=\pi S\omega_B/B$. The last equation may be integrated easily and we obtain, as well as in the high temperature limit, $t$ as a function of the soliton velocity,

$$\mathcal{T}(y)\approx 0.07\ln\left\{\frac{y_1-y}{y_1-y_0}\sqrt{\frac{10y_0^2-y_0+0.8}{10y^2-y+0.8}}\right\} -0.3[\arctan(3.6y-0.03)-\arctan(3.6y_0-0.03)]. \tag{48}$$

Here $\mathcal{T}=5Gt$ denotes the time measured in the dimensionless units, $y_0=v_0/2c_0$ ($v_0$ denotes the initial soliton velocity) while $y_1=1.2$ represents the only real root of the third order polynomial in the right-hand side of Eq. (46). The desired time dependence of the soliton velocity may be obtained by inverting this relation. It is visualized in Fig. 5 where we have plotted the dependence of the soliton velocity, measured in units $2c_0$, on dimensionless time $\mathcal{T}=5Gt$. It follows that the soliton velocity gradually decreases and after the finite time $\mathcal{T}_0=\mathcal{T}(y=0)$ it approaches zero. From Fig. 5 we easily estimate this; let us call it the stopping time, as $\mathcal{T}_0\sim v_0/2c_0$ or in real units $t_0\sim(v_0/2c_0)(B/\pi S\omega_B)$.

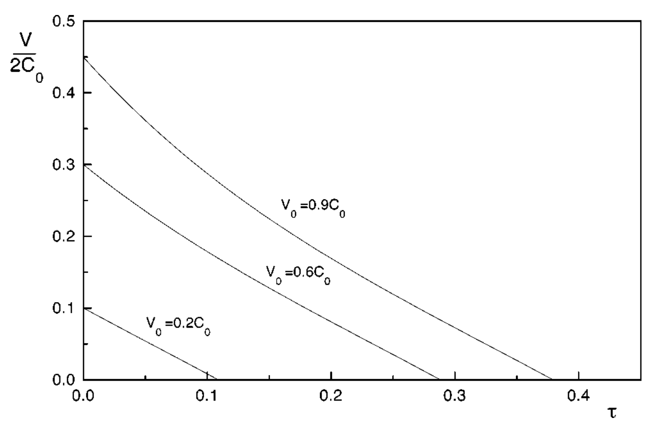


FIG. 5. Soliton velocity in units of $v_0$ versus the dimensionless time $\mathcal{T}$. Low temperature limit.

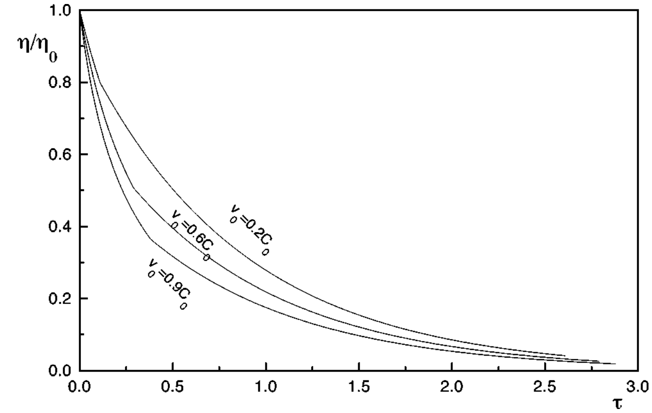


FIG. 6. Decay of the soliton amplitude versus the dimensionless time $\mathcal{T}$. Low temperature limit.

In order to find the time dependence of the soliton amplitude we shall use an auxiliary relation

$$\ln\frac{\eta}{\eta_0}=-1.183\mathcal{T}(y)+1.087\ln\frac{y_1-y_0}{y_1-y} -0.028\ln\frac{10y^2-y+0.8}{10y_0^2-y_0+0.8}. \tag{49}$$

By virtue of this relation and the explicit expression for $\mathcal{T}(y)$ one may find, numerically, the desired time evolution of the soliton amplitude. It is visualized in Fig. 6 for the three values of $v_0$.

Like in the high temperature case the soliton amplitude exhibits exponential decay which now substantially depends on its velocity. Namely, we observe that the soliton at rest is comparably more stable than the moving one. In particular, when its velocity approaches zero the relatively rapid decay of the soliton amplitude transits into a somewhat slower, pure exponential one,

$$\eta=\eta(\tau_0)e^{-\mathcal{T}}. \tag{50}$$

From this relation we estimate the soliton half-life time as

$$\tau_{1/2}\sim\frac{\ln 2B}{5\pi S\omega_B}. \tag{51}$$

## IV. CONCLUSION

Concluding this paper we note that our analysis shows that, due to the coupling with phonons, a multiquanta soliton radiates energy (excitons) which induces its slowing down and the gradual decay of its amplitude. As a consequence the soliton lifetime is finite and determined by the values of the basic physical parameters of system (coupling constant and adiabaticity parameter) and temperature. This enables one to determine, more precisely than in [19], the relevance of the multiquanta soliton mechanism for the intramolecular vibrational energy transfer in molecular chains. Namely, the soliton lifetime should be long enough in order to transport energy over large distances. This imposes certain demands on the values of the system parameters. As could be expected the rate of the soliton decay is strongly influenced by the value of the coupling constant which must be very small in order to provide sufficient stability of these excitations. However, according to the soliton existence condition (5), the smallness of the coupling constant is already assumed if such solitons could be formed at all. Therefore, in order to discuss the stability of the particular soliton created of the $\mathcal{N}$ quanta, it is more convenient to express the soliton lifetime through the number of quanta participating in its formation. In such a way, taking into account relation (5), we may rewrite Eqs. (42) and (51), respectively, as $\tau_{1/2} \sim 5.65(\mathcal{N}/TB) \times 10^{-13}$ s and $\tau_{1/2} \sim \mathcal{N}\omega_B^{-1}$. As one can see, the soliton stability at low temperatures is comparably better than on the high ones. On the basis of these results we are now in a position to estimate the possible role of the multiquanta soliton in the transport processes for the concrete system. Using the set of parameters which is usually quoted as the representative for the $\alpha$ helix and related molecules (ACN, for example), we found that $B \sim 0.14 - 0.16$, $E_B = (10^{-23} - 10^{-22})J$, and $S \sim 0.01 - 0.1$. These values correspond to the nonadiabatic and weak coupling limit, where, in principle, such solitons may be formed [19]. For these substances at 300 K, $k_B T/\hbar\omega_B \sim 1.95 - 2.27$, so that $\tau_{1/2}$ must be estimated in accordance with Eq. (42) so that we have $\tau_{1/2} \sim 10^{-13}$ s.

Our results seriously question the possible role of multiquanta solitons in the particular biological context. Namely, our estimate for the multiquanta soliton lifetime, at finite temperatures, is of the same order as previously found by Cottingham and Schweitzer [14] and Schweitzer [15] who discussed the lifetime of the single particle Davydov soliton (i.e., the soliton created on account of the single vibron ST). Therefore, our conclusion is that, as well as the original Davydov proposal, the multiquanta soliton is not a likely candidate for the intramolecular vibrational energy transfer in biological systems in realistic conditions. However, while the original concept fails due to its inherent inconsistency [16–18], i.e., a single particle soliton cannot be formed at all for the given conditions (nonadiabatic limit), the creation of the multiquanta soliton in principle is quite possible; however, even if formed such excitation lives too short to be useful in biological processes. This, however, does not exclude the relevance of such a mechanism of vibrational energy transfer in different contexts. This can be seen from our estimates of the soliton stopping and lifetime at low temperatures which may be of a few orders of magnitude larger than in the high temperature regime. Namely, for the macromolecules with a wider phonon bandwidth, polyacetylene for example ($\hbar\omega_B \sim 10^{-20}$ $J$), which is high compared with the thermal energy ($k_B T$) at 300 K, the soliton lifetime should be estimated by Eq. (51) and therefore could be at least of two orders of magnitude longer than in the $\alpha$ helix and ACN.

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[1] T. Uzer, with an appendix by W. H. Miller, Phys. Rep. **199**, 73 (1991).
[2] E. G. Petrov, *Physics of Charge Transfer in Biological Systems* (Naukova Dumka, Kiev, 1984).
[3] *Coherent Excitations in Biological Systms*, edited by H. Fröhlich and F. Kremer (Springer, Berlin, 1983).
[4] H. Haken, *Information and Selforganization* (Springer, Berlin, 1986).
[5] D. E. Green, Science **181**, 583 (1973).
[6] C. W. F. McClare, Nature (London) **240**, 88 (1972).
[7] A. S. Davydov and N. I. Kislukha, Phys. Status Solidi B **59**, 465 (1973).
[8] A. S. Davydov and N. I. Kislukha, Zh. Éksp. Teor. Fiz. **71**, 1090 (1976) [Sov. Phys. JETP **44**, 571 (1976)].
[9] See, for example, *Davidov's Soliton Revisited*, edited by P. L. Christiansen and A. C. Scott (Plenum, New York, 1990).
[10] A. C. Scott, Phys. Rep. **217**, 1 (1992).
[11] D. M. Alexander, Phys. Rev. Lett. **54**, 138 (1985).
[12] D. M. Alexander and J. A. Krumhansl, Phys. Rev. B **33**, 7172 (1986).
[13] W. Förner, J. Phys.: Condens. Matter **4**, 1915 (1992).
[14] J. P. Cottingham and J. W. Schweitzer, Phys. Rev. Lett. **62**, 1792 (1989).
[15] J. W. Schweitzer, Phys. Rev. A **45**, 8914 (1992).
[16] D. W. Brown and Z. Ivić, Phys. Rev. B **40**, 9876 (1989).
[17] D. W. Brown, K. Lindenberg, and X. Wang, in *Davidov's Soliton Revisited*, edited by P. L. Christiansen and A. C. Scott (Plenum, New York, 1990).
[18] Z. Ivić, D. Kapor, M. Škrinjar, and Z. Popović, Phys. Rev. B **48**, 3721 (1993).
[19] Z. Ivić, D. Kostić, Ž. Pržulj, and D. Kapor, J. Phys.: Condens. Matter **9**, 413 (1997).
[20] J. Tekić, Z. Ivić, and Ž. Pržulj, J. Phys.: Condens. Matter **10**, 1487 (1998).
[21] J. Tekić, Z. Ivić, S. Zeković, and Ž. Pržulj, Phys. Rev. E **60**, 821 (1999).
[22] Yu. Kivshar and B. Malomed, Rev. Mod. Phys. **61**, 763 (1989).
[23] F. G. Bass, Yu. Kivshar, V. V. Konotop, and Yu. A. Sinitsyn, Phys. Rep. **157**, 63 (1989).
[24] N. Flytzanis, Z. Ivić, and B. A. Malomed, J. Phys.: Condens. Matter **7**, 7843 (1995).
[25] B. A. Malomed, Phys. Scr. **38**, 66 (1988).
[26] A. S. Davydov and A. V. Zolotariuk, Phys. Scr. **28**, 249 (1983).